



EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND

ECBC-TR-174

**INVESTIGATION OF POLYURETHANE ADHESIVES
FOR USE IN THE APACHE AVIATOR NBC PROTECTIVE MASK**

**Gerald P. Young
Steven Ciborowski
David May
Lawrence Oswald
Steven Gross**

ENGINEERING DIRECTORATE

August 2001

**Approved for public release;
distribution is unlimited**



Aberdeen Proving Ground, MD 21010-5424

20011011 113

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 2001 August		3. REPORT TYPE AND DATES COVERED Final; 00 Sep - 01 Feb
4. TITLE AND SUBTITLE Investigation of Polyurethane Adhesives for Use in the Apache Aviator NBC Protective Mask			5. FUNDING NUMBERS PR-62262255200	
6. AUTHOR(S) Young, Gerald P.; Ciborowski, Steven; May, David; Oswald, Lawrence; and Gross, Steven				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ECBC, ATTN: AMSSB-REN-EM, APG, MD 21010-5424			8. PERFORMING ORGANIZATION REPORT NUMBER ECBC-TR-174	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release: distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Polyurethane adhesives are currently used in Apache aviator masks to secure polycarbonate lenses to a bromobutyl-natural rubber face piece. An alternative polyurethane adhesive packaged in a pre-measured assembly was investigated to determine its suitability for mask remanufacturing operations. Seventy-five prototype assemblies were prepared with the standard and alternative adhesive. The composite assemblies were then destructively tested on an Instron machine, in tension, to compare rupture strength of the polycarbonate-adhesive-rubber joint as a function of curing regime and surface preparation. Rupture load measurements indicate the alternative adhesive investigated is adequate for securing lenses within the aviator mask. Stress applied at joint failure ranged from 146 to 343 pounds per square inch. Prototypes cured at 63 degrees Celsius are approximately 38% stronger than ambient cured specimens.				
14. SUBJECT TERMS Polyurethanes Rupture strength Adhesives			15. NUMBER OF PAGES 19	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Blank

PREFACE

The work described in this report was authorized under Project No. 62262255200. This work was started in September 2000 and completed in February 2001.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Center.

Acknowledgment

The authors gratefully acknowledge the U.S. Army Edgewood Chemical Biological Center experimental fabrication shop for assistance with design and fabrication of test prototypes.

Blank

CONTENTS

1.	INTRODUCTION.....	7
2.	MATERIALS AND METHODS.....	9
3.	RESULTS.....	15
4.	CONCLUSIONS	16
	LITERATURE CITED	19

FIGURES

1.	Configuration of Prototypes.....	10
2.	Load to Rupture Plastic-Adhesive-Rubber Joint.....	11
3.	Rubber Delamination: Specimen in Instron Machine.....	15
4.	Rupture Strength Comparison.....	17
5.	Rupture Strength: Polycarbonate-Polyurethane-Rubber Joints.....	18

INVESTIGATION OF POLYURETHANE ADHESIVES FOR USE IN THE APACHE AVIATOR NBC PROTECTIVE MASK

1. INTRODUCTION

Adhesives have a long history of use in human artifacts. Studies by the Weizmann Institute of Science reveal that in the stone age, humans were putting organic compounds to use to join dissimilar materials together. As far as 8,000-years-ago Neolithic cavemen who lived in the area of the Dead Sea were producing a form of collagen glue, as an adhesive to hold together tools, utensils, and ceremonial artifacts that included *decorated skulls*.¹

Natural glues and resins derived from animal and plant sources were used extensively from antiquity up to the early 20th century. It is known that the ancient Egyptians used collagen in its gelatinous form as the basis for the "carpenter's glue" to hold together furniture.

With the advent of the industrial revolution and the establishment of a chemical process industry, adhesives began to be derived as adjuncts to a wide range of compounds derived from petrochemical sources.

In the Apache Aviator Mask, Polyurethane is used as a material to bond polycarbonate lenses to a facepiece that is composed of a blend of natural and bromobutyl rubbers.

There is probably no more versatile material for so many high-performance applications than polyurethane. With a molecular structure composed of four of the most common elements - carbon, hydrogen, oxygen, and nitrogen - polyurethane has a combination of properties which are not available in any other thermoplastic material including excellent resistance to ozone, weak bases, fuels and oils.

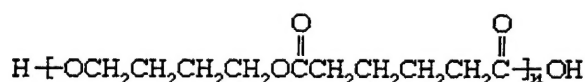
Urethane was first introduced in 1849 by Germany's Wurtz and Hoffman, when they presented the chemical reaction between Isocyanate and Hydroxyl.²

The precursors were initially limited to Diisocyanate and Polyester; however, the industry began looking for different Hydroxyl Polyols due to problems with processability, cost, foaming physical properties, etc. By 1957, various Polyether Polyols were being produced, offering not only cost effectiveness but also anti-foaming physical properties. Thereafter, the Urethane Industry was able to make leaping advances with the development of silicone surfactants.

Polyurethanes are a class of extremely versatile polymers that are made into flexible and rigid foams, fibres, elastomers, and surface coatings. They are formed by reacting an isocyanate (a compound having the functional group NCO) with an alcohol (having the functional group OH).

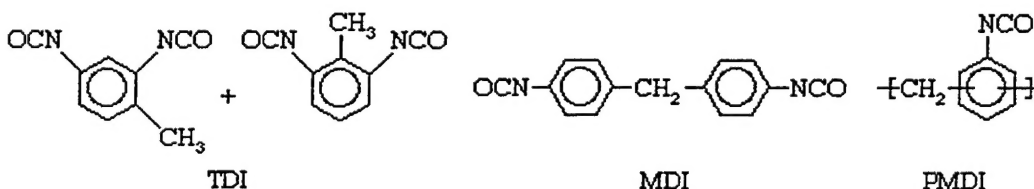
Polyurethane molecules can adopt a linear or a network architecture. Linear polyurethanes are formed by reacting a dialcohol with a diisocyanate, whereas network

polyurethanes are formed from polyfunctional alcohols or isocyanates. Dialcohol monomers include ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$); diethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$); 1,4-butanediol ($\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$); 1,6-hexanediol ($\text{HO}[\text{CH}_2]_6\text{OH}$); alcohol-terminated polyethers such as polyethylene oxide and polypropylene oxide (see Aliphatic polyethers); and flexible, alcohol-terminated polyesters such as poly-1,4-butylene adipate:



The alcohol-terminated polyethers and polyesters are known as polyols.

Isocyanates commonly used to prepare polyurethanes are toluene diisocyanate (TDI), methylene-4,4'-diphenyl diisocyanate (MDI), and a polymeric isocyanate (PMDI). These isocyanates have the following structures:



During the late 1930s Otto Bayer, manager of the IG Farben laboratories in Leverkusen, Ger., prepared many polyurethanes by condensation reaction of dihydric alcohols such as 1,4-butanediol with difunctional diisocyanates. A major breakthrough in the commercial application of polyurethane did not occur until 1941, when a trace of moisture reacted with isocyanate to produce carbon dioxide. The production of this gas resulted in many small empty areas, or cells, in the product (which was subsequently called "imitation Swiss cheese"). In 1953 Bayer and the Monsanto Chemical Company (now Monsanto Company) formed the Mobay Chemical Corporation to produce polyurethane in the United States.³

Urethane is a product of Hydroxyl compounds such as Polyether Polyols and polymerized derivatives of Isocyanates. Urethane's unique chemical structure is the result of supplemental reactions between the Polyisocyanate and Polyol(activation hydrides).

The external characteristics of the polyurethane end-products vary, resulting in diverse characteristics such as marshmallow-like softness to concrete-hardness, or rubber-like stretchability that allows the product to stretch to 10-times its size to materials that offer almost no change in form. Additionally, Urethane, as a comfort and convenience-providing material, is used in a wide range of applications in automobiles, electronics,

furnishings, architecture, etc. because they offer unique qualities relative to other general high molecular compounds.⁴

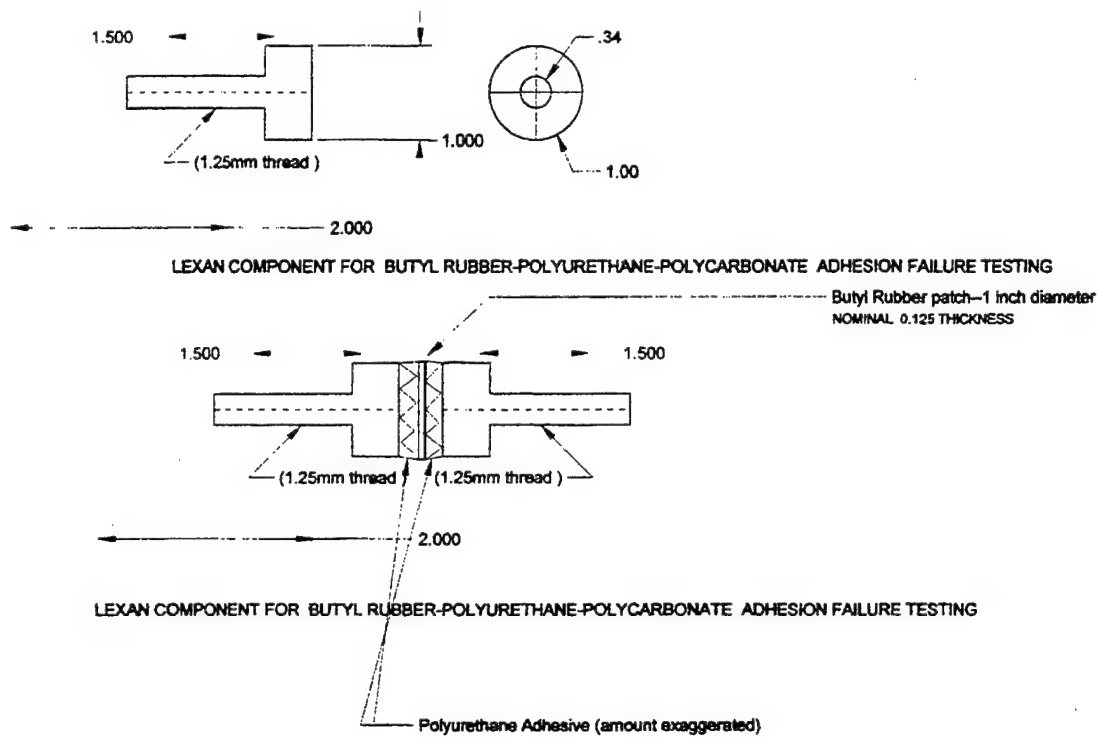
In the Apache Aviator Mask, polyurethane adhesives are critical materials for joining dissimilar materials together and providing chemically resistant, mechanically tough bonds and joints. In this study, two polyurethane adhesives cured at elevated and ambient temperature and with different surface preparations are compared. As a measure of the effectiveness of the adhesives, the bond rupture strengths were measured for the various rubber-polyurethane adhesive-polycarbonate plastic joints. The rupture strength data will serve as a basis for the substitution of adhesives in planned mask maintenance, upgrade, and repair operations where lens replacement will be required.

2. MATERIALS AND METHODS

Test items consisting of one-inch diameter right circular cylindrical blocks of polycarbonate, stamped circular rubber coins and polyurethane adhesive were assembled. The polycarbonate substrates were machined from polycarbonate 1-inch diameter rod with a 1.5-inch stem (Figure 1) using ASTM 429 as a general guide to the configuration of test specimens.

Once machined, the polycarbonate pieces were sanded with either with 80 or 100 grit aluminum oxide sand paper, and cleaned with isopropyl alcohol solution (99% by volume) to remove any residual polycarbonate dust or grit left on the surface from the sand paper. The surfaces were coated with LORD 7701 adhesion promotion solution (consisting of a mixture of ethyl acetate and alcohols), followed by drying for several minutes while resting on absorbent paper. The stamped rubber coins were also sanded with 80 or 100 grit sand paper, followed by cleaning with isopropyl alcohol solution and application of the LORD 7701 adhesion promoter. The individual components were then assembled in groups, which were differentiated by the use of either LORD 7500 (Figure 2) adhesive or LORD 7540 adhesive. In any assembly the polycarbonate surfaces were all either 100 grit sanded or 80 grit sanded. Some rubber coins were not sanded to determine the impact of no rubber surface preparation on joint rupture strength.

Lord 7500 adhesive is a two part adhesive consisting of a black, extraordinarily viscous polyol, which must be mixed with a cream colored isocyanate mixture in the proportion of 1 part by weight polyol to 1.7 parts isocyanate. The resulting mixture then appears a light gray color and depending on degree of mixing will sometimes display variegated strands of lighter and darker colors. Good mixing of the components results in a visually uniform color without dark and light striations. The useful life of this mixture is exceedingly short, on the order of 10 minutes or less. The reaction between polyol and isocyanate quickly proceeds to the point where it is impractical to apply the adhesive since it becomes extraordinarily viscous and too difficult to apply.

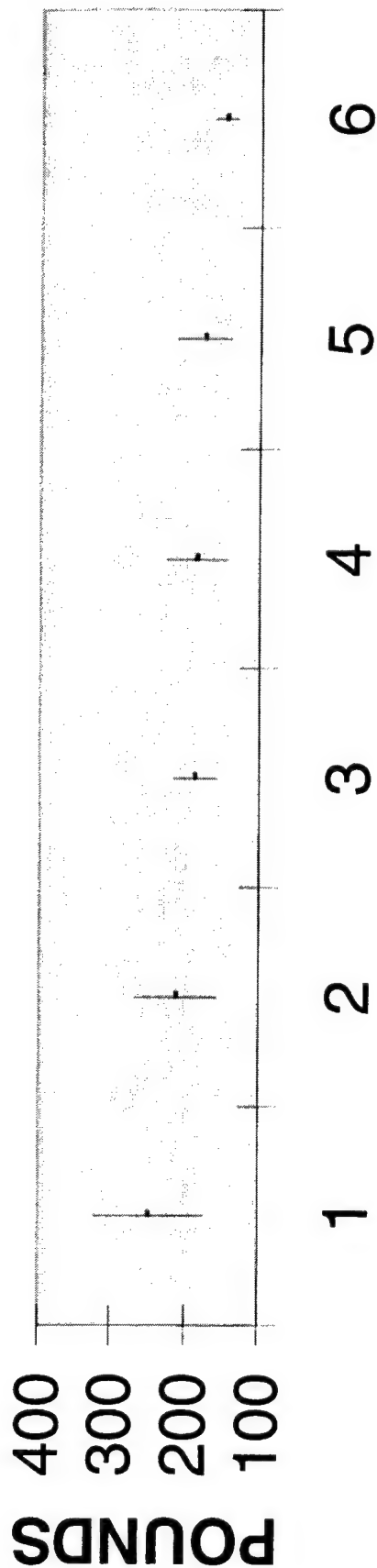


LEXAN OPTICAL GRADE 141R-111

DeltaCad DEMO

Figure 1: Configuration of Prototypes

RUPTURE STRENGTH OF ADHESIVE BONDS

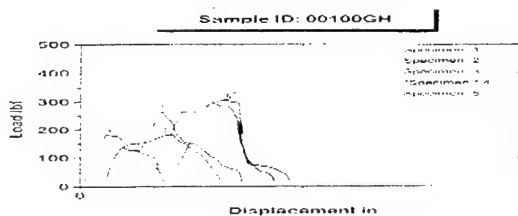


ADHESIVE, SURFACE PREP, CURE TEMP.
COMBINATIONS

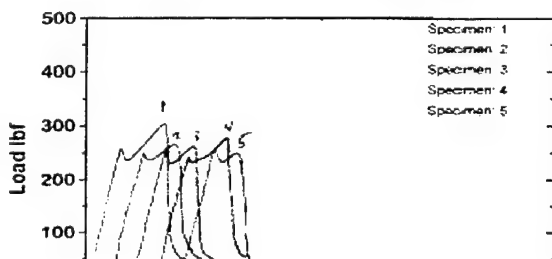
Figure 2: Load to Rupture Plastic-Adhesive-Rubber Joint

LEGEND

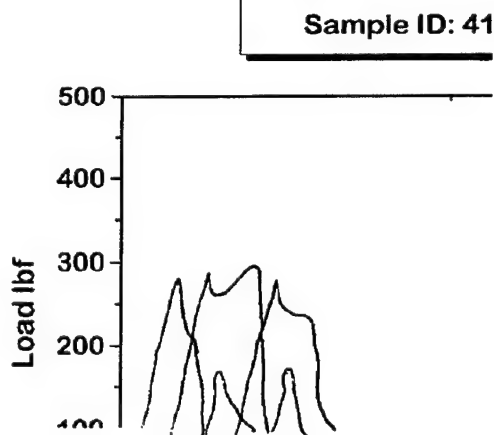
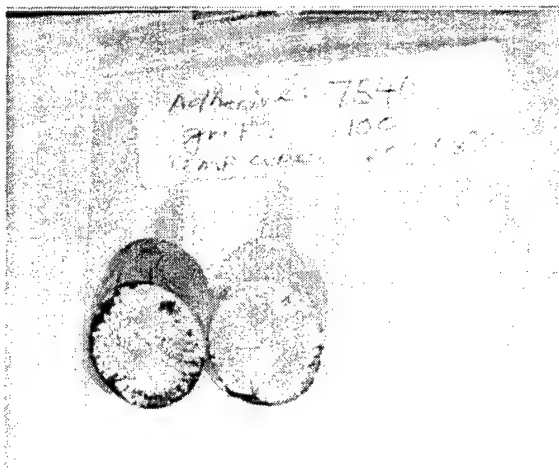
	<u>GROUP</u>	<u>SURFACE</u>	<u>CURING</u>	<u>RUPTURE MODE</u>	<u>Load at Rupture</u>
	<u>ADHESIVE</u>	<u>PREPARATION</u>	<u>TEMP.</u>		<u>(Lbs)</u>
2-1	7500	100 Grit	63 Celsius	Rubber Tearing	249+/-73



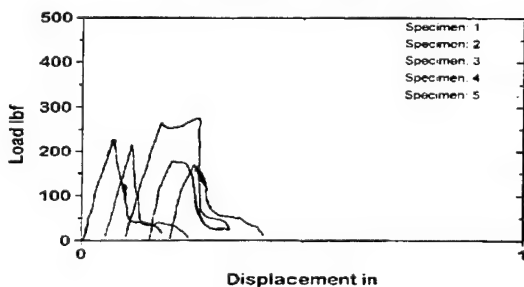
Sample ID: 5100GH



2-2	7540	100 Grit	63 Celsius	Adhesive Tearing from Polycarbonate	213+/-54
-----	------	----------	------------	-------------------------------------	----------



Sample ID: 40100GH



2-3 7540

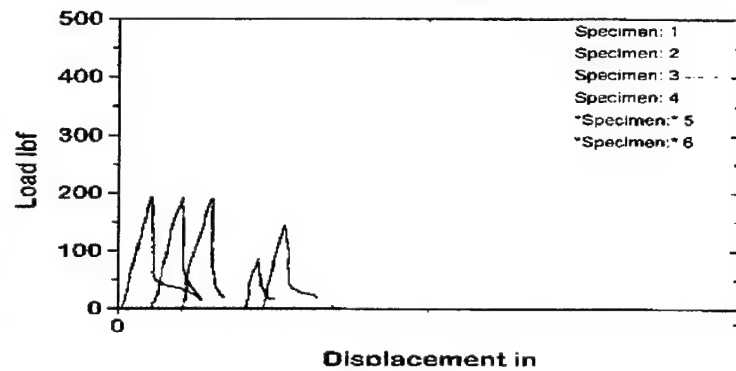
100 Grit

Ambient

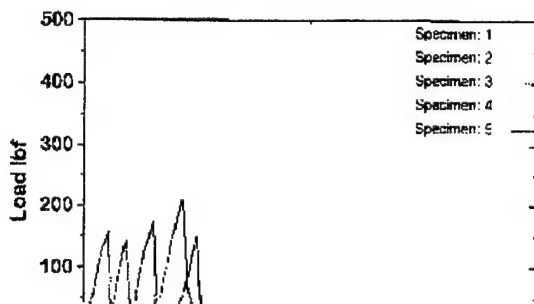
Rubber Delaminates
from Adhesive

188+/-28

Sample ID: 40100GA



Sample ID: 4100GA



2-4 7500

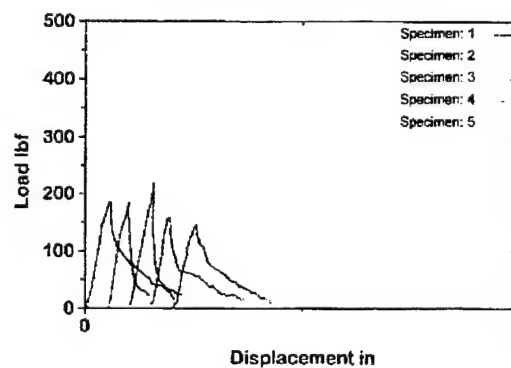
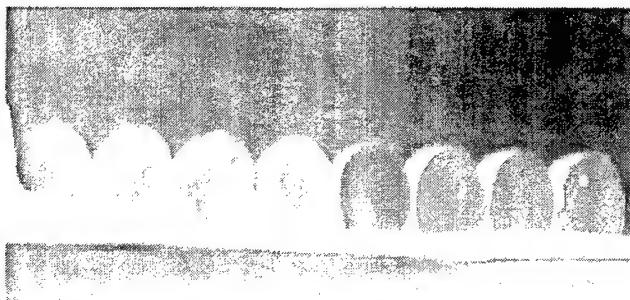
100 Grit

Ambient

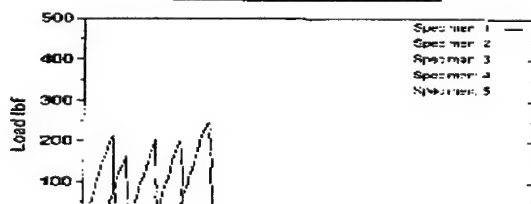
Rubber Delaminates
from Adhesive

186+/-40

Sample ID: 00100GA



Sample ID: 5100GA



2-5 7540

80 Grit

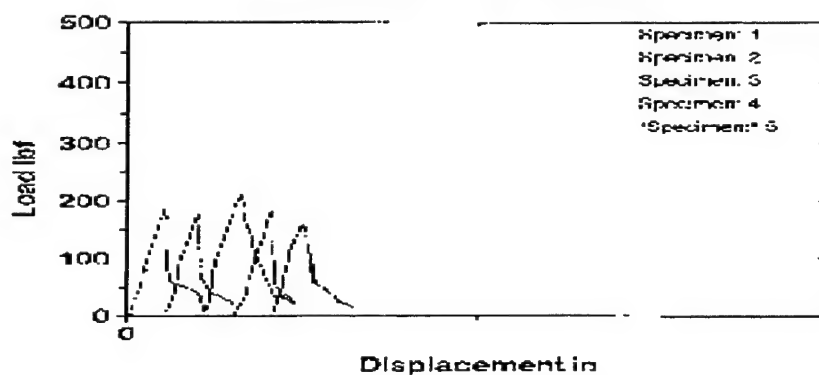
Ambient

Rubber Delaminates
from Adhesive

177+/-36



Sample ID: 4080GA



2-6 7500

80 Grit

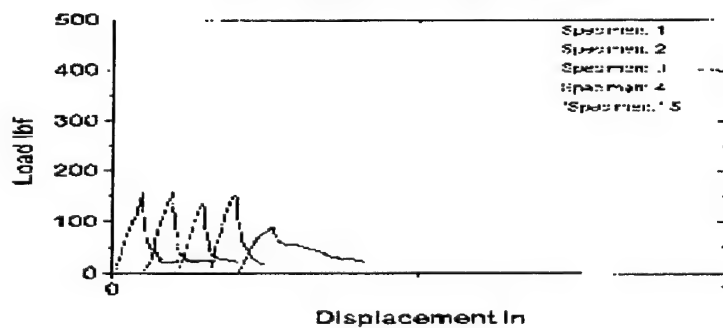
Ambient

Rubber Delaminates
from Adhesive

149+/-15



Sample ID: 0080GA



Lord 7540 adhesive is also a two part polyurethane system, however it is manufactured in pre-measured applicator tubes, which are designed for use in a glue gun. A static mixing element is attached to the outlet of the cartridge to blend the two components. In this application the ratio of components appears to be 1 to 1 as both preloaded tubes are of equal diameter. The 7540 adhesive, when well mixed, is also a light gray color.

Approximately 0.1 cubic centimeter of adhesive is applied to each face of the polycarbonate and then spread between the two-polycarbonate mating surfaces. Once both surfaces were covered with the adhesive the prepared rubber coins were inserted between the polycarbonate cylinders, compressed together by hand, excess adhesive removed and the joined components set in a 1 inch inner diameter plastic tube which acted as a jig to keep the parts from slipping apart or sliding out of alignment during curing. Ten Specimens prepared with 7500 adhesive were then cured in a 63 degrees Celsius convection oven for 24 hours. Ten assemblies prepared with 7540 adhesive were also cured in the convection oven at 63 degrees Celsius for 24 hours. All the remaining assemblies were allowed to cure for a minimum of 48 hours at room temperature.

3. RESULTS

The following rupture load results were obtained when the test specimens were placed under tensile stress in the Instron apparatus (Figure 3).

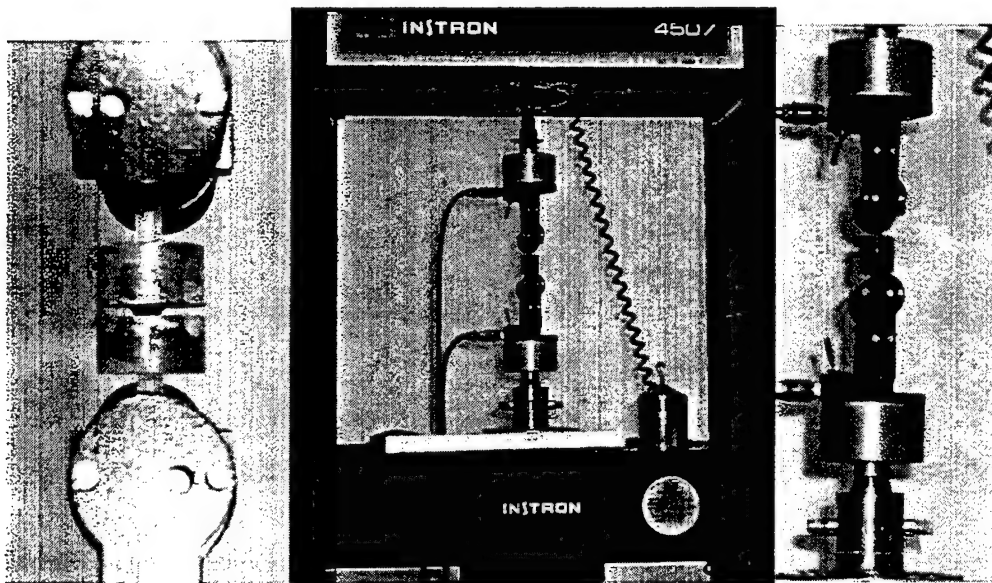


Figure 3. Rubber Delamination: Specimen in Instron Machine

4. CONCLUSIONS

One-inch diameter right circular cylindrical Polycarbonate-Rubber joints can be effectively bonded with polyurethane adhesives. Preparation of the polycarbonate surface includes sanding with 100 or 80 grit aluminum oxide sand paper, cleaning and removal of grit and abraded polycarbonate with commercially available over-the-counter isopropyl alcohol followed by treatment with an ethyl acetate-based adhesion promoter such as Lord Product 7701. Rubber surfaces can also be pretreated with 100 or 80 grit papers or no sanding as long as adhesion promoter is applied to the rubber prior to application of uncured polyurethane adhesive.

The measurements show that joints of rubber and polycarbonate bonded with Lord Polyurethane Adhesive 7500 fail under loads that are approximately equivalent to the loads (Figure 4), which cause failure in rubber-polycarbonate joints bonded with Lord Adhesive 7540, as long as the surface preparations and curing regimes are equivalent. Curing the specimens at 63 degrees Celsius for a period of 18 to 24 hours appears to strengthen the bonds. Surface treatment and abrasion of the rubber in specimens cured at elevated temperature seems to improve the bond strength, but only minimally from 3% to 6%.

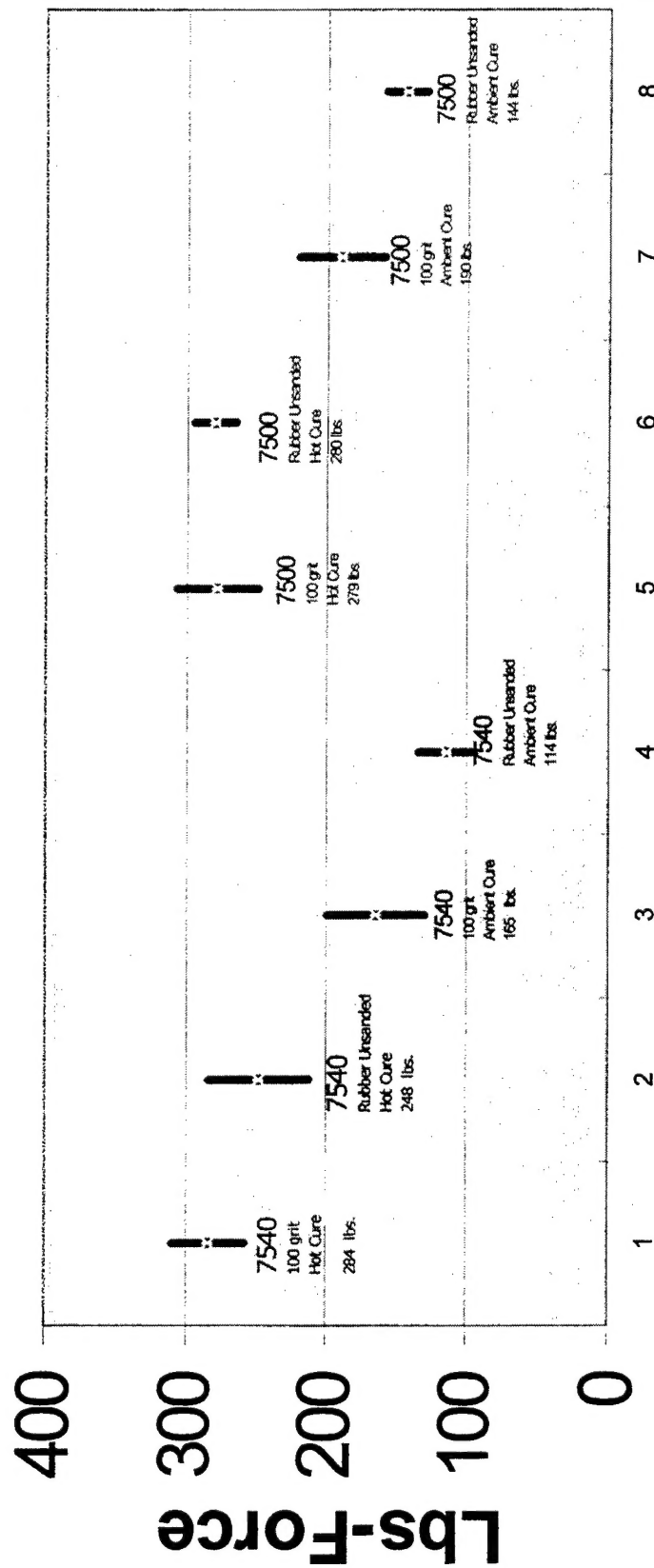
Surface treatment of rubber seems to have a stronger effect on improving bond strength in specimens that are not subjected to elevated temperature curing and are allowed to cure under ambient conditions for several days. The average increase in bond strength for surface treated and abraded rubber in ambient cured specimens ranges from 38% to 58%. The overall bond strength of ambient cured (20 degrees Celsius) specimens irrespective of surface treatment is significantly less than those cured at 63 degrees Celsius, on the order of 38% weaker than oven cured samples (Figure 5).

The following table summarizes the results obtained:

Adhesive	Rubber Surface Preparation	Cure Condition	Predominant Joint Failure Mode	Stress applied at joint failure Range
7540	None	Ambient	Rubber cleanly delaminates from adhesive with little rubber tearing	146psi +/-18%
7500	80 Grit	Ambient	Rubber delaminates from adhesive with Small areas of Rubber Tearing	174psi +/-26%
7500	None	Ambient	Rubber delaminates from adhesive	182psi +/-9%
7540	100 grit	Ambient	Rubber delaminates from adhesive	217psi +/-11%
7540	80 Grit	Ambient	Rubber delaminates from adhesive	231psi +/-15%
7500	100 grit	Ambient	Rubber delaminates from adhesive	249psi +/-11%
7540	None	63C Cure	Large area of rubber tearing	315psi +/-14%
7500	None	63C Cure	Rubber tearing	333psi +/-12%
7540	100 grit	63C Cure	Adhesive tearing from polycarbonate	333psi +/-20%
7500	100 grit	63C Cure	Rubber tearing	343psi +/-8%

Figure 4. Rupture Strength Comparison

13 Feb 2001 Data

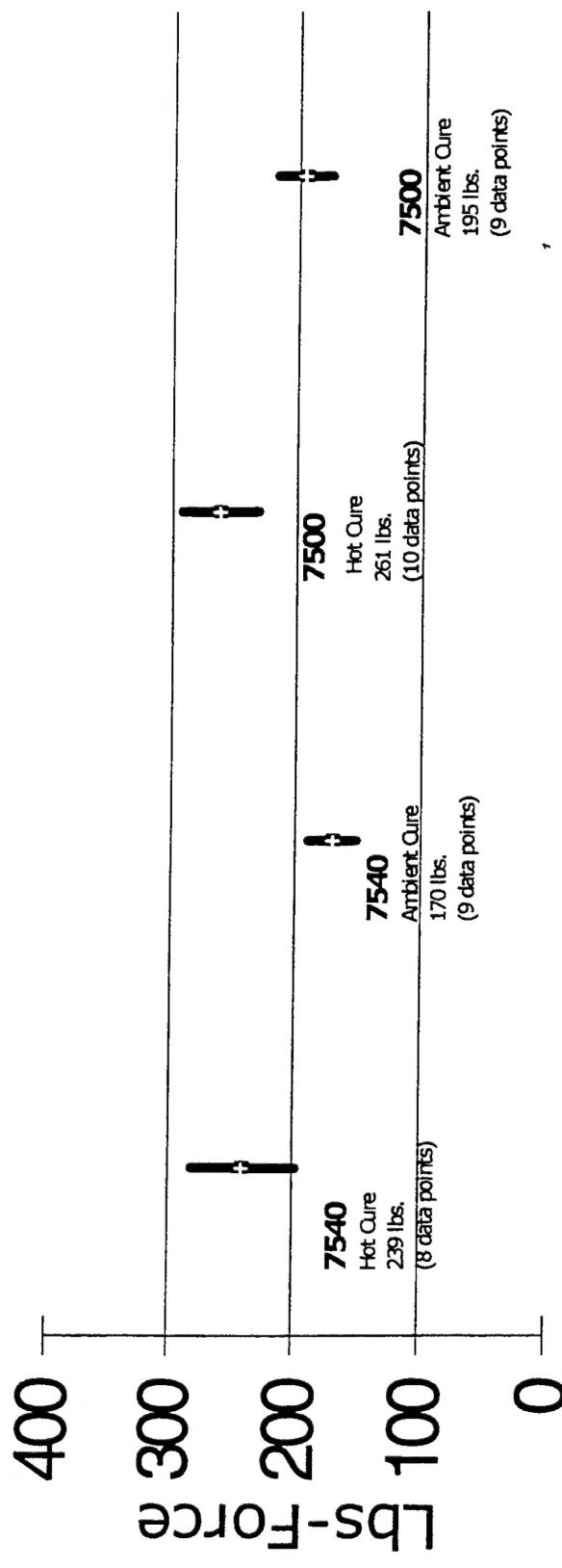


7540 vs. 7500 Adhesive

Hot cure Temperature: 63 C

Ambient Cure Temperature: 20 C

Figure 5. Rupture Strength: Polycarbonate-Polyurethane-Rubber Joints



7540 vs. 7500 Adhesive
Hot cure: 63 C Ambient Cure: 23 C
January and February 2001 Data
100 grit surface treatments

LITERATURE CITED

¹ *These findings, reported in the Hebrew-language Archeologia Umada'ei Hateva ("Archaeology and Natural Sciences"), add a new chapter to the history of adhesives and to humankind's technological history in general. (An English translation of the paper is available, as are color slides of the ancient decorated skulls).*

² Organic Chemistry, Hendrickson J.B.; Cram D.J.; Hammond G.S., McGraw Hill Series in Chemistry, 1970.

³ Encyclopaedia Britannica Online, Polyurethane Entry.

⁴ Modern Adhesives, McGraw-Hill Science Press, 1998